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CRDEC-TR-083

USE OF TIME-DEPENDENT CHEMICAL SENSOR SIGNALS  
FOR SELECTIVE IDENTIFICATION

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June 1989

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS										
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.										
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE												
4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-083		5. MONITORING ORGANIZATION REPORT NUMBER(S)										
6a. NAME OF PERFORMING ORGANIZATION See Reverse	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION										
6c. ADDRESS (City, State, and ZIP Code) See Reverse		7b. ADDRESS (City, State, and ZIP Code)										
8a. NAME OF FUNDING/SPONSORING ORGANIZATION CRDEC	8b. OFFICE SYMBOL (if applicable) SMCCR-RSL	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER										
8c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423		10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO.</td><td>PROJECT NO.</td><td>TASK NO.</td><td>WORK UNIT ACCESSION NO.</td></tr><tr><td>1C161102</td><td></td><td>A71A</td><td></td></tr></table>		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.	1C161102		A71A		
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.									
1C161102		A71A										
11. TITLE (Include Security Classification) Use of Time-Dependent Chemical Sensor Signals for Selective Identification												
12. PERSONAL AUTHORS (S) (see reverse)												
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 86 Oct TO 87 Sep	14. DATE OF REPORT (Year, Month, Day) 1989 June	15. PAGE COUNT 26									
16. SUPPLEMENTARY NOTATION												
17. COSATI CODES <table border="1"><tr><th>FIELD</th><th>GROUP</th><th>SUB-GROUP</th></tr><tr><td>07</td><td>04</td><td></td></tr><tr><td></td><td></td><td></td></tr></table>		FIELD	GROUP	SUB-GROUP	07	04					18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Microsensors, Time-dependent sensor Electrochemical sensor Activation energy	
FIELD	GROUP	SUB-GROUP										
07	04											
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>A sensor system is described for identifying and quantifying different components in a gas mixture by decoding information from a modulated output signal. The system operates by passing the unknown gas into a reaction chamber containing a heated catalytic filament. The output products of the chamber are detected by an electrochemical sensor. The concentration of the reaction products is modulated by varying the temperature of the catalytic filament. A theory is presented for analyzing the modulated output signal. The validity of the analysis is confirmed by experiments conducted with benzene, CO, HCN, and by computer simulations. It appears possible to identify different species in the inlet gas stream if the species undergo chemical reactions in the reactor that have different activation energies. The signal magnitude at peaks or valleys in the output is directly proportional to concentrations even though a steady state condition is not reached. The approach may be generalized to other detector systems.</p>												
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED										
22a. NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON		22b. TELEPHONE (Include Area Code) (301) 671-2914	22c. OFFICE SYMBOL SMCCR-SPS-T									

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

**6. NAMES AND ADDRESSES OF PERFORMING ORGANIZATIONS (continued)**

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## PREFACE

The work described in this report was authorized under Project No. 1C161102A71A, Research in CW/CB Defense. This work was started in October 1986 and completed in September 1987.

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## USE OF TIME-DEPENDENT CHEMICAL SENSOR SIGNALS FOR SELECTIVE IDENTIFICATION

### 1. INTRODUCTION

The magnitude of a sensor response at steady state is commonly used to determine the species concentration; whereas, the information in the transient response is generally not processed. However, the transient signal can be made to contain information that can identify and quantify the chemical species present. In this report, a purposely caused, periodic, nonsteady-state sensor signal is generated, and this modulated signal is controlled experimentally to provide information about specific chemical species present and their concentrations.<sup>1-3</sup>

Modulated systems have been employed in multiplex gas chromatography in which multiple samples are injected, the column temperature is modulated, and the cross-correlation of the resulting chromatogram is computed.<sup>4-6</sup> A variety of modulated detectors have been reported recently, including a mass-flow modulated, flame ionization detector;<sup>7</sup> a temperature-modulated, thermal conductivity detector;<sup>8</sup> a temperature-modulated, array of MOS gas detectors;<sup>9</sup> and a solute-modulated, electron capture detector.<sup>10</sup> In all of these detectors, the information content of the complex signal is higher, and the speed of data acquisition is greater than in corresponding signals obtained using conventional systems.<sup>11</sup> Synchronous detection of modulated signals also can improve the signal-to-noise (S/N) ratio because low frequency noise and drift are not modulated and, therefore, can be eliminated from the amplified signal.

A theory has been developed for an existing sensor system,<sup>1-3</sup> and measurements were made to aid in model development. The system consists of a reaction chamber and an electrochemical cell (Figure 1). The gas to be analyzed is exposed to the electrically heated catalytic filament in the reaction chamber that precedes the detector. The rate at which the chemical reaction proceeds depends on the species concentration, catalyst activity, and chamber residence time. After leaving the reaction chamber, the products of reaction are detected by an electrochemical sensor that produces an output proportional to the product concentration. The product concentration can be controlled most easily, in this case, by changing the temperature of catalyst or the flow rate (i.e., residence time of the analyte in the reactor).

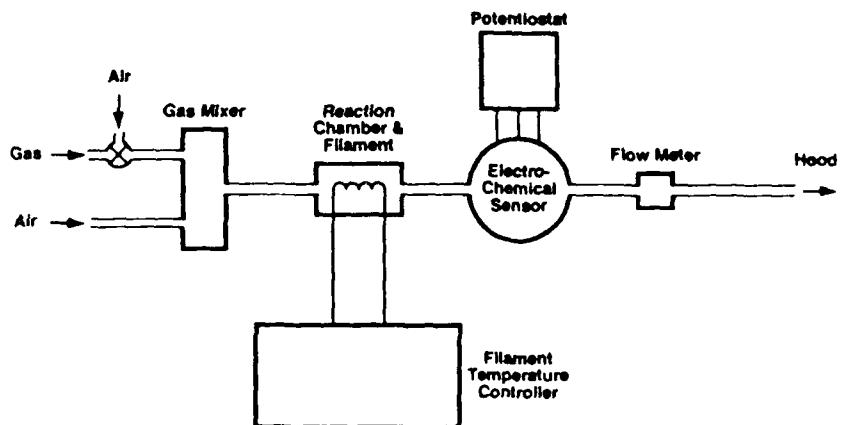


Figure 1. Detector System.

The transient response of the sensor is expressed in terms of the volume ( $V_0$ ) of the reaction chamber, the reaction rate constant ( $k$ ), the concentration [ $C(t)$ ] of the molecules detected by the sensor, the time constant of the electrochemical sensor ( $\tau_s$ ), and the absolute sensor sensitivity ( $m$ ) in the microamperes per parts per million. Measurements were made under two different conditions using low concentrations of cyclohexane and benzene in air. One condition is with a fixed filament temperature, and the other condition is with a periodic modulation of the filament temperature, producing a constant concentration and a periodic modulation in the concentration of the reactant species, respectively. By making transient measurements at different flow rates, the parameters characterizing the system response were determined, and models for the system operation were developed.

## 2. THEORETICAL ANALYSIS

### 2.1 Model of Electrochemical Sensor.

An equivalent circuit model proposed for the electrochemical sensor is shown in Figure 2. This model assumes that the electrochemical cell is a linear amperometric sensor with a steady-state output current [ $i_s(t)$ ] proportional to the concentration [ $C(t)$ ]:

$$i_s(t) = m' C(t) \quad (1a)$$

and the current [ $i(t)$ ] measured by the potentiostat detector circuit is proportional to the voltage [ $V(t)$ ]:

$$i(t) = V(t) \times G \quad (1b)$$

where  $G$  is constant. Implicit in equation 1b is the assumption that the response time of the potentiostat is much shorter than the response time of the electrochemical cell. The general solution for  $i(t)$  is

$$i(t) = \left[ \frac{me^{-t/\tau_s}}{\tau_s} \right] \int C(t') e^{-t'/\tau_s} dt' \quad (2)$$

where

$$C(t) = 0 \text{ for } t < 0$$

$m = m'RG$  = intrinsic sensitivity of cell

$\tau_s = RC$  = sensor time constant

If the number of moles of gas in  $V_0$  increases from 0 to  $n_c$  at  $t = 0$ , the resulting current response is

$$i(t) = m(n_c/V_0)(1 - e^{-t/\tau_s}) \quad (3a)$$

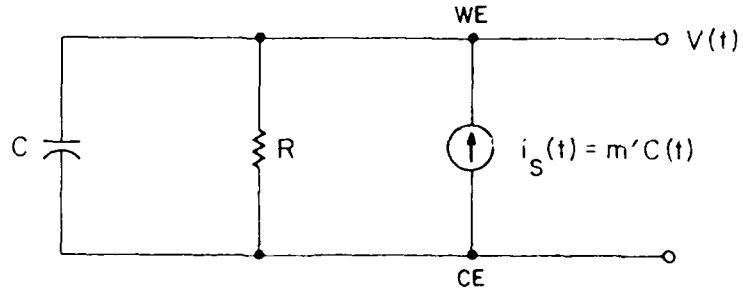


Figure 2. Equivalent Circuit for the Electrochemical Cell. CE is the counter electrode; WE is the working electrode;  $i_s(t)$  is the Faradaic current; R and C are the internal resistance and capacitance of the electrochemical cell.

One interesting consequence of this circuit model is that the potentiostat output  $i(t)$  is directly proportional to the instantaneous concentration  $C(t)$  whenever  $dC(t)/dt = 0$ . This condition occurs at steady state as well as at the output peaks and valleys that occur during periodic modulation of the analyte concentration. To prove that the output is directly

proportional to the concentration, we note that the current  $i_s(t)$  in the circuit shown in Figure 1 is given by

$$i_s(t) = \frac{V}{R} + \frac{1}{C} \times \frac{dV}{dt} \quad (3b)$$

When  $di(t)/dt = 0$ , it follows from equation 1b that  $dV(t)/dt = 0$ . Therefore, no current flows through the capacitor, and from equation 3b, it follows that

$$i_s(t) = \frac{V(t)}{R} \quad (3c)$$

Using this result and equation 1a, we can find that the sensor output will be proportional to the concentration whenever  $di(t)/dt = 0$ :

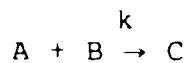
$$i(t) = mC(t) \text{ when } di(t)/dt=0 \quad (3d)$$

This condition occurs at steady state or at peaks and valleys in the modulated sensor signal.

Figure 3 shows the effect of  $\tau_s$  on  $i(t)$  when the input concentration is varied sinusoidally at a frequency  $\omega$ . The peak at which output current shifts from the peak of the input by an amount equal to  $\tan^{-1}(\omega\tau_s)$ , and the output current is reduced by the factor  $[1 + (\omega\tau_s)^2]^{-1/2}$ . Curve (a) in Figure 3 tracks the input concentration almost exactly. This model predicts that the sensor response time must be significantly smaller than the period of modulation to insure an adequate signal. Faster sensors will allow higher modulation frequencies for given signal amplitudes. The electrochemical sensor may not be an ideal detector in their kind of sensor system.

## 2.2 Model of Reaction Chamber Dynamics.

Input gas, with component species A and B, flows into the reaction chamber of  $V_0$  at a rate of  $u$  (liters per second). A reaction takes place in which a reactant C is formed



where  $k$  is the reaction rate constant (liters per mole-second). The gas in the chamber, which is assumed to be homogeneous and isothermal, exits into an electrochemical sensor where it is detected. The chamber contains a fixed amount of catalyst. It is assumed that the gas has returned to the ambient temperature when it reaches the sensor and that the flow through the sensor is fixed.

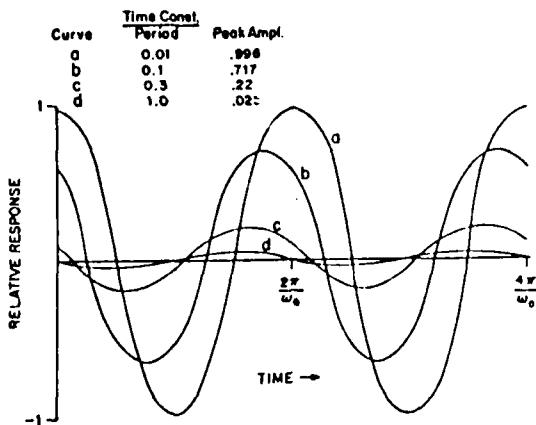


Figure 3. Electrochemical Cell Output for a Periodic Variation in Concentration with Frequency  $\omega = 2\pi/T$  for Different Ratios of the Cell Time Constant to the Period  $\tau_0/T$ : (a) 0.01, (b) 0.1, (c) 0.3, and (d) 1.0.

The reaction rate  $r(t)$  (moles per liter-second) is directly proportional to the concentrations of the reactants:

$$r = k \left( \frac{n_a}{V_0} \right) \left( \frac{n_b}{V_0} \right) \quad (4)$$

In the typical trace pollutant detection problem, the concentration of the species to be detected (species A) is several hundred parts per million whereas the oxygen concentration is 200,000 ppm. To solve the system of coupled first-order, nonlinear differential equations describing the process in the reaction chamber, we assume the following:

- The change in the concentration of oxygen due to the reaction is negligible.
- The nitrogen is an inert diluent gas and does not affect the form of the equations.
- The flow of air into  $V_0$  equals the flow out (total flow in = total flow out).

The expressions obtained for  $n_c(t)$ , the number of moles of species C in  $V_0$ , are parameterized in terms of the residence time  $\tau_{res}$  and the characteristic chemical reaction time  $\tau_a$  where

$$\tau_{res} = \frac{V_0}{u} \quad (5a)$$

and  $u$  = flow rate of sample gas into chamber (liter per second)  
and

$$\tau_a = V_o / (kn_b) \quad (5b)$$

The reaction rate ( $r$ ) can be written in terms of  $\tau_a$ :

$$r = (n_a / V_o) (1/\tau_a) \quad (6)$$

The reaction rate constant ( $k$ ) is assumed to depend on temperature only:

$$k = A \exp(-\Delta E / R_G T) \quad (7)$$

where

$A$  = pre-exponential factor for the particular oxidation

$\Delta E$  = activation energy for conversion of A to C

$R_G$  = gas constant per mole

In the Arrhenius equation, the pre-exponential typically has a square root dependence on temperature<sup>12</sup> (neglected in our analysis).

In the following paragraphs, solutions for  $n_c(t)$ , the modulated concentration, are determined for two cases.

### 2.2.1 Case 1 (Constant Temperature).

When the filament in the reaction chamber is held at a constant temperature, for a step function change in the number of moles of species A into  $V_o$  at time  $t = 0$ , we find:

$$n_r(t) = n_a \frac{\tau_{res}}{\tau_{res} + \tau_a} (1 - e^{-t/\tau^*}) \quad (8)$$

where

$$(\tau^*)^{-1} = (\tau_{res})^{-1} + (\tau_a)^{-1} \quad (9)$$

The equation for  $(\tau^*)^{-1}$  can be interpreted as representing the sum of the number of moles per second due to the flow plus the

number of moles per second due to the reaction. The steady-state solution (as  $t \rightarrow \infty$ ) is:

$$n_c(\infty) = \frac{n_a \tau_{res}}{(\tau_{res} + \tau_a)} \quad (10a)$$

$$n_c(\infty) = k \frac{n_a n_b}{(u + k n_b)} \quad (10b)$$

### 2.2.2 Case 2 (Time-Dependent Filament Temperature).

Variation of the temperature with time produces exponential variations in the reaction rate. The following general integral expression for  $n(t)$  can be written for this case:

$$n(t) = \frac{\int_0^t e^{\int dt/\tau} \cdot r(t) dt}{e^{\int dt/\tau}} \quad (11)$$

### 2.3 Model for the Detection System.

The model for the detection system is developed through a joint consideration of the sensor model response and the time-dependent production of analyte C in the reaction chamber. The expression for the output current from the electrochemical sensor is obtained by substituting the appropriate equation for the concentration of the oxidation product C into equation 1 for the sensor response. For the constant temperature case, with a step function change in the number of moles of A in the reaction chamber at  $t = 0$ , we obtain:

$$i(t) = m \left( \frac{\tau_{res}}{\tau_{res} + \tau_a} \right) \left( \frac{n_a}{V_o} \right) \left( 1 - \frac{\tau_s}{\tau - \tau_s} e^{-t/\tau_s} - \frac{\tau'}{\tau - \tau_s} e^{-t/\tau'} \right) \quad (12)$$

The first term in parentheses on the right-hand side of the equation represents the fraction of A converted to C [the conversion ratio (R)]. The second term represents the initial concentration of A in the reaction chamber, and the last term yields the time dependence. At steady state, this last term goes to unity as  $t \rightarrow \infty$ . The conversion ratio (R) can be written using equation 5:

$$R = (1 + u/(k n_b))^{-1} \quad (13)$$

Note that  $R$  depends on the flow rate ( $u$ ) and the reaction rate ( $k$ ) but is independent of cell volume ( $V_o$ ). Therefore, steady-state measurements can give information about  $m$  and  $k$  but not about  $\tau_s$  or  $V_o$ . The constant  $m$  is characteristic of the sensor sensitivity for a given oxidation product, and  $k$  is characteristic of the analyte for a given catalyst and reaction chamber condition.

To obtain values for these parameters, we fit solutions for  $i(t)$  to measurements taken at various flow rates. At very low flow rates,  $R$  goes to unity, and all of the reactant A is converted to C. Conversely, at high flow rates, the conversion is low, and  $R$  is given by:

$$R = (kn_b)(1/u), \text{ for } u \text{ large} \quad (14)$$

Therefore, plots of the steady-state current  $i(\infty)$  can be used to identify the region of operation and the behavior of the system as shown in Figure 4. The constants  $m$  and  $k$  can be obtained from the steady-state data by plotting the inverse of the steady-state signal per unit concentration  $(n_a/V_o)[1/i(\infty)]$  versus  $u$  since

$$(n_a/V_o)(1/i(\infty)) = (1/m)(1+u/kn_b) \quad (15)$$

Data acquired at a low flow rate can be used to determine  $m$ . To determine the activation energy ( $\Delta E$ ), measurements must be made at two or more different temperatures. The remaining parameters  $V_o$  and  $\tau_s$  must be determined by fitting transient measurements to the theoretical expressions for  $i(t)$ . The mathematical expressions are simplified if the measurements are made in either a fast or slow flow regime.

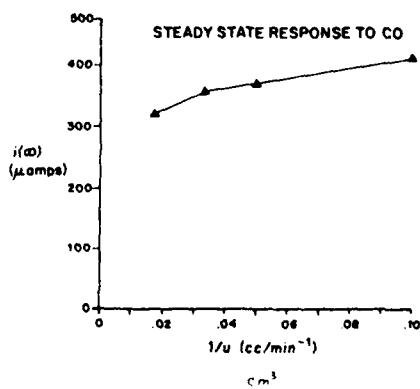


Figure 4. Steady-State Output Current Versus Inverse of the Flow Rate  $u$ .

2.4 Use of Periodic Filament Temperature Variations in the Detection System.

From the above consideration, we are now prepared to investigate how a periodic variation (e.g., sinusoidal) in the filament temperature can yield information that can assist in differentiating between different species that produce detectable reaction products (C) from reactions with different rates (e.g., different rate constants and activation energies). For simplicity in this analysis, we assume that the variations in temperature T about  $T_0$  that are given, for example, by

$$T = \Delta T \sin(\omega t + \phi) + T_0 \quad (16)$$

are sufficiently slow so that the solution for the steady-state current (equations 15 and 13) is

$$i(\infty) = mC_a R \quad (17)$$

where  $C_a = n_a/V_0$  is valid for all times during the temperature cycle. This condition will be met if the period of the modulation is much greater than  $\tau^*$ .

We can write a two-term Taylor series expansion for the steady-state current as a function of the filament temperature (T)

$$i(\infty, T) = i(\infty) \Big|_{T_0} + \frac{di(\infty)}{dT} \Big|_{T_0} \Delta T \quad (18)$$

The first term on the right represents the dc current ( $i_{dc}$ ). The second term represents the ac current magnitude ( $i_{ac}$ ) in the small signal approximation in which all higher order terms in  $\Delta T$  have been omitted in equation 18. This approximation will be valid provided

$$\frac{i_{ac}}{i_{dc}} = \frac{1}{i(\infty)} \frac{di(\infty)}{dT} \Delta T \ll 1 \quad (19)$$

Differentiating equation 17, we obtain

$$i_{ac} \equiv \Delta T \frac{di(\infty)}{dT} \Big|_{T_0} = mC_a R (1 - R) \frac{\Delta E}{R_a T} \frac{\Delta T}{T} \quad (20)$$

Because  $0 < R < 1$  for any finite nonzero flow, it follows that the derivative in equation 20 never vanishes; thus, there is always an ac response. Because  $i(\infty) = i_{dc}$ , from equation 18, it follows that

$$\frac{i_{ac}}{i_{dc}} = (1-R) \frac{\Delta E}{R_G T} \frac{\Delta T}{T} \quad (21)$$

This ratio is independent of concentration and, therefore, carries the qualitative information required to identify the reacting species A. The ratio depends only on the flow rate,  $\Delta T$ , and  $\Delta E$ . Therefore, it should be possible to distinguish between reactions and components with different activation energies.

The magnitude of the dc signal varies directly with R (equation 17); whereas, the ratio of the ac to dc signal goes as  $1-R$ . Therefore, at low conversions, the dc signal is reduced, but the ratio of the ac to dc signal is increased. For a typical case ( $\Delta E = 30$  kcal/mole,  $T = 900$  K,  $T = 10$  °C), we find that  $i_{ac}/i_{dc}$  varies from 0.18 for 10% conversion to 0.10 for 50% conversion.

The operating point [ $P_o$  (u, T)] at which the ac signal is a maximum can be determined by computing a second derivative and setting it equal to zero

$$\frac{di_{ac}}{dT} \Big|_{P_o} = \frac{d^2 i(\infty)}{dT^2} \Big|_{P_o} = 0 \quad (22)$$

This yields a condition on the dc signal for which the ac signal is a maximum:

$$i(\infty) \Big|_{P_o} = -\frac{mC_a}{2} \left[ 1 - \frac{2R_G T}{\Delta E} \right] \quad (23)$$

The peak in the ac curve corresponds to a dc conversion ratio slightly less than 50%:

$$R \Big|_{P_o} = \frac{1}{2} - \frac{R_G T}{\Delta E} \quad (24)$$

For the previous numerical example  $R|_{P_o} = 0.45$ . The physical significance of equation 24 becomes apparent by noting from equations 5a and 5b that

$$\frac{\tau_a}{\tau_{res}} = \frac{u}{kn_b} \quad (25)$$

Therefore, at  $P_0$ , it follows that

$$\frac{\tau_a}{\tau_{res}} = \frac{1/2 + R_G T / \Delta E}{1/2 - R_G T / \Delta E} \geq 1 \quad (26)$$

For most practical values of  $T$  and  $\Delta E$ , it follows that  $\tau_a = \tau_{res}$  at  $P_0$ . Therefore, the ac signal is at its peak when the characteristic reaction time approximately equals the residence time.

## 2.5 Analysis of Gas Mixtures.

If there are independent noninterferring species present and the system response to each is linear, gas mixtures can be analyzed by the described detector system. It is more likely that such approximations will be valid if low concentrations and conversion ratios are maintained.

### 2.5.1 Constant Filament Temperature.

A sensitivity  $S_{ij}$  (ampere per parts per million) for the species  $i$  at temperature  $T_j$  and flow rate  $u_j$  can be defined as:

$$S_{ij} = \frac{i_i(\infty)}{C_i} \Big|_{T_j, u_j} \quad (27)$$

where  $C_i = n_i/V_0$  is the concentration of species  $i$ . Generalizing our previous result (equation 15) yields:

$$S_{ij} = m_i(1 + u_j/k_i n_b)^{-1} \quad (28)$$

If the term  $S_{ij}$  is determined for each species, under a set of flow rate and temperature conditions, the total steady-state response at condition  $j$  is

$$I_j(\infty) = \sum_i C_i S_{ij} \quad (29)$$

To solve for the concentration of each species ( $C_i$ ,  $i = 1, \dots, n$ ), calibration measurements must be made to determine  $S_{ij}$  at  $n$  different sets of conditions  $j = 1, \dots, n$ . The sensitivity  $S_{ij}$  is a square matrix that can be inverted to find the  $C_i$ . To invert  $S$ , the coefficients for  $S_{ij}$  must be different for different species ( $i = 1, \dots, n$ ) at the same conditions (fixed  $j$ ) and be different for the same species (fixed  $i$ ) at different conditions. Also, elements of  $S_{ij}$  must be large enough to permit accurate computations.

### 2.5.2 Periodic Variation of Filament Temperature.

Generalizing equation 20 to several independent species indicated by the subscript "i," and using equation 13 for R, we obtain an expression for the total ac response at conditions  $(u_j, T_j)$ :

$$i_{acj}(\infty) = \Delta T \sum_i C_i s_{ij} \quad (30)$$

where

$$s_{ij} = m_i \left[ \frac{\Delta E_i}{R_G T^2} \right] \left[ \frac{u/k_i n_b}{(u/k_i n_b + 1)^2} \right]_{T=T_j, u=u_j} \quad (31)$$

The factor  $s_{ij}$  is dependent on the temperature,  $u$ , and  $\Delta E_i$ . To ensure that we can solve the system of equations,  $s_{ij}$  must obey the same restrictions as  $S_{ij}$ .

### 3. MODEL VALIDATION

Figure 5 shows the response of the electrochemical sensor to 20 ppm CO/air gas mixture (CO sensor, ND, model 110, Pittsburgh, PA). The sensor gave a response time constant of 5.71 s, a sensitivity of 3.75 A/ppm, and operates consistently with the model proposed (Figure 1 and equation 3a). Data for CO taken at different flow rates agreed with equation 15.1-3. In Figure 6, the response of the electrochemical sensor is shown at different frequencies of the filament temperature cycles of the reactor filament when a benzene air mixture is introduced. The amplitude of the temperature cycle is from 650 to 870 °C. The oscillation is damped due to the slow sensor response (Figure 3) or to the slow filament response at the higher frequencies. At low frequencies, the steady-state response  $i(\infty)$  is nearly achieved at each temperature extreme.

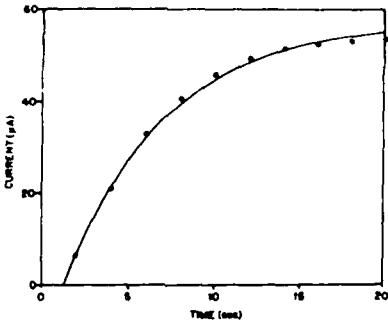


Figure 5. Sensor Response to CO. Solid line is best exponential fit of the form of equation 3a.

An experiment similar to that shown in Figure 6 was performed for HCN in which the amplitudes at the top and bottom of the peaks (called "A" and "B," respectively) were studied. A consequence of the sensor model is that the signal should be proportional to the concentration whenever  $di/dt = 0$  (Section 2.1). This condition is met at the peaks and valleys. The model is validated by the observations (Figure 7), and linear response is obtained for this sensor system even though it is not at steady state.

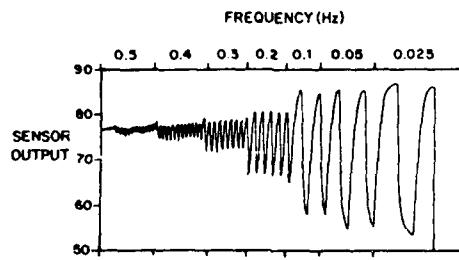


Figure 6. Electrochemical Cell Response to 511 ppm Benzene/Air at Different Filament Frequencies with Square Wave Power Input, Temperature Variation Between 650 and 870 °C,  $u = 120 \text{ cm}^3/\text{min}$ ,  $V_o = 1 \text{ cm}^3$ .

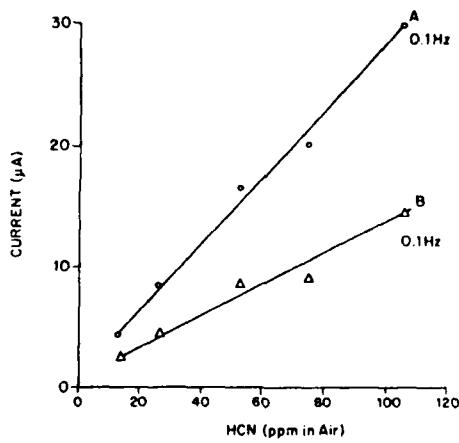


Figure 7. Linearity of Transient Part of Sensor Response Versus Concentration of HCN. "A" and "B" represent peaks and valleys, respectively.

The steady-state detector response versus temperature is shown in Figure 8 for 512 ppm of benzene. The curve represents the best fit of equation 15 to the first 5 data points. The drop in response at high temperatures is not predicted by the theory, but the theory is valid at the lower temperatures. A reduction in oxidation rate at increasing temperature suggests a more complex reaction mechanism than can be explained by Langmuir-Hinshelwood kinetics.<sup>13</sup> The theory could be extended to include these mechanisms, but it is easier to restrict our discussion to temperatures below 700 °C where our model is operative.

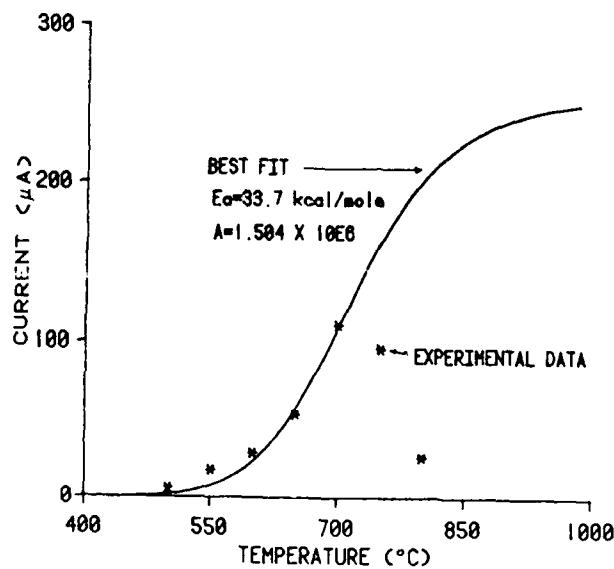
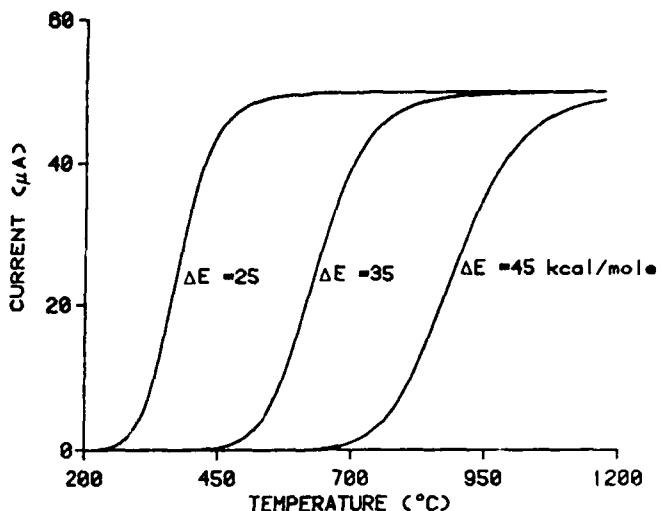


Figure 8. Current Versus Temperature Data for 511 ppm Benzene. The solid line is the best fit to equation 15.

Assuming the data for benzene is representative of other species, equation 15 can be used to simulate the steady-state sensor response to changes in the reaction rate due to changes in  $\Delta E$  (i.e., species) and the filament temperature (i.e., rate constant). In Figure 9, the calculated steady-state current is plotted as a function of temperature for three different chemical species that have three different  $\Delta E$ . A response of  $50/\mu A$  represents 100% conversion of A to C ( $m = 0.5 A/ppm$ ). The position of the  $i$  versus  $T$  curves is very dependent on  $\Delta E$ . This dependency suggests the possibility of discrimination between species with different reaction rates.



$$u = 1 \text{ cm}^3/\text{min} \text{ and } A = 1.5 \times 10^6 \text{ cm}^3/\text{mole-s}$$

Figure 9. Calculated Current Versus Temperature Curves for Three Different Activation Energies ( $\Delta E$ ),  $u = 1 \text{ cm}^3/\text{min}$ ,  $A = 1.5 \times 10^6 \text{ cm}^3/\text{mole-s}$ .

Figure 10 illustrates a simulation of the sensor response to a mixture of species with the  $\Delta E$  ( $\Delta E = 25, 35$ , and  $45 \text{ kcal/mole}$ ) used in Figure 9. Because it is assumed that the chemicals give independent responses, Figure 10 is simply the sum of the individual curves from Figure 9. When the derivative, with respect to temperature, is taken of the mixture curve, a "spectrum" is obtained with peaks corresponding to different activation energies (Figure 11). The peak heights correspond to the magnitude of the ac sensor response, and the location of the peak identifies  $P_0$  and  $T_0$  at which the sensor exhibits the greater temperature dependence for the species with that particular  $\Delta E_0$  (equations 20 and 22). This kind of "spectrum" could be generated experimentally by modulating the temperature in a sine wave while also ramping the temperature from low to high and using phase sensitive detection to monitor only the modulated sensor response.

Modulation of the filament temperature about  $T_0$  should not produce a modulated sensor signal for species with  $\Delta E$  significantly different from  $\Delta E_0$ . This is illustrated in Figure 12 where the temperature is modulated in a sine wave about  $T_0$  for a species with a  $\Delta E_0$  of  $33.7 \text{ kcal/mole}$  (and  $A = 1.5 \times 10^6 \text{ cm}^3/\text{mole-s}$ ). The calculated sensor response shows very little ac component for compounds with  $\Delta E$  of  $25$  and  $40 \text{ kcal/mole}$ . The absolute current scale depends on the sensitivity of the sensor. The conversion rate of  $\Delta E = 25 \text{ kcal/mole}$  is  $0.99$ ; and at  $\Delta E = 33.7 \text{ kcal/mole}$ , the ac signal is a maximum.

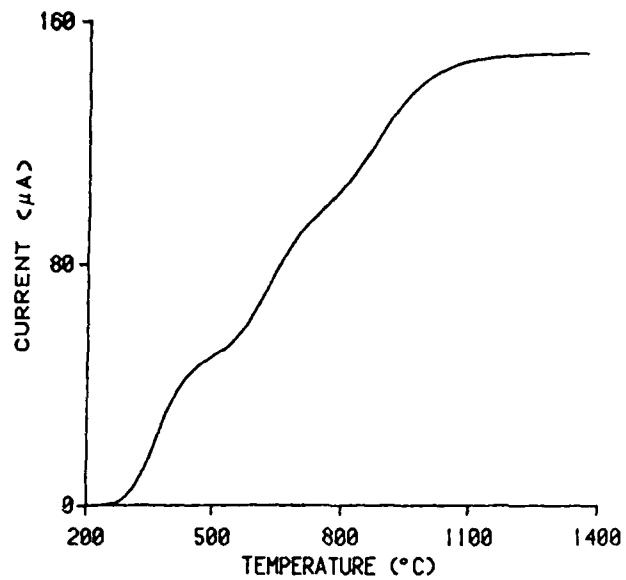


Figure 10. Calculated Steady-State Sensor Response to a Mixture of Species with Activation Energies of 25, 35, and 45 kcal/mole (from Figure 9).

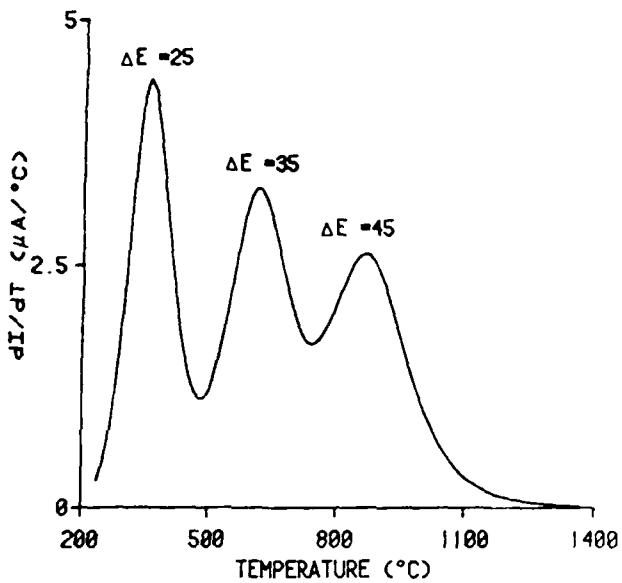


Figure 11. Derivative of the Response Curve in Figure 10 with Respect to Temperature T. The derivative is proportional to the magnitude of the ac sensor response to a small sinusoidal variation of the filament temperature.

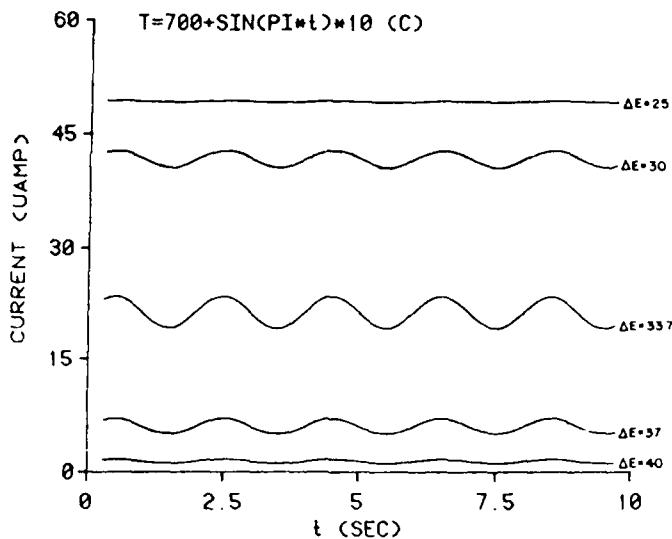


Figure 12. Calculated Response of Sensor for Activation Energies from 25 to 40 kcal/mole. The filament temperature varies sinusoidally from 690 to 710 °C with a period of 2 s.

The simulations have assumed that the pre-exponential term is the same for each species, and the differences in rate constants are due solely to differences in activation energies. This is obviously not always a valid assumption. One can also expect the pre-exponential term A to vary from species to species, which will also cause the current versus temperature curves to shift. However, the greatest discrimination with temperature variation will result from differences in  $\Delta E$  because  $\Delta E$  appears in the exponent of the rate constant. The ac simulations assume that temperature variations are sufficiently slow that equation 15 remains valid (i.e., steady-state currents are observed). This assumption was made for mathematical simplicity and could be eliminated by use of equation 11.

#### 4. CONCLUSIONS

A model has been constructed to analyze the output current from a detection system that includes a modulator of concentration and a detector. Specific responses have been discussed for a system consisting of a reaction chamber with a heated catalytic filament and an electrochemical sensor. The parameters required to apply the theory can be obtained by system operation at different flow rates and temperatures. Theory predicts that periodic modulated reaction rates can be of use in identifying and quantifying gases alone and in mixtures. Initial data for our detector system with HCN and benzene and

computer simulations confirm certain aspects of the model and outline its limitations. In particular, it appears possible to determine concentrations using appropriate measurements taken before steady state is reached. Therefore, by using the approach proposed, the response time for concentration measurements from a given sensor can be reduced. A "smart" sensor that cycles rapidly at high concentrations can immediately detect dangerous situations; whereas, one that cycles slowly at low concentrations achieves maximum sensitivity. The measurement accuracy may be reduced using ac methods if the dc signal/noise ratio is excellent. On the other hand, if significant low frequency noise or drift is present, the use of synchronous ac detection may be more accurate.

More extensive experimentation will be required to validate and refine the model so that practical applications can be realized for various concentration-modulated systems. Some potential advantages of using nonsteady-state responses from a detector for chemical analysis include faster response, greater dynamic range, and the ability to carry quantitative and qualitative information about several species on a wave form type output. The filament/catalyst and electrochemical sensor system may be too slow to explore the full potential of the approach outlined herein.

The computer simulations and theoretical analyses appear to indicate that the appropriate choice of filament temperature, amplitude of temperature modulation, and flow rate will result in the "filtering out" of responses from all species with significantly different rate constants than that of a selected compound to be detected by the sensor system. Experiments are now required to determine the actual variability of  $k$  and  $\Delta E$  from species to species. A more general sensor response model should be incorporated into the theory, and faster modulator/detector pairs should be studied to validate the above arguments.

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